PATENT SPECIFICATION (11) 1 445 989

1 445 989

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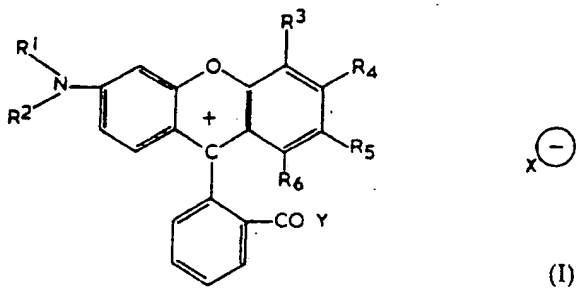
(19)

(54) COLOURATION PROCESS

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the colouration of synthetic polymeric materials in particular polymeric materials comprising polymers and copolymers of acrylonitrile by the application thereto of a certain class of dyestuffs of the fluoran series.

Thus according to the present invention there is provided a process for the colouration of synthetic polymeric materials in particular polymers or copolymers of acrylonitrile which comprises applying thereto a dyestuff of the general Formula I



(I)

wherein R^1 is hydrogen or an optionally substituted alkyl group, R^2 is an optionally substituted aryl group, preferably optionally substituted phenyl, R^3, R^5 and R^6 are independently chosen from hydrogen, optionally substituted alkyl, aralkyl or aryl groups, acyl, alkoxy, aryloxy, halogen, cyano, nitro, or a group of the formula $-COOR^7$, $CONR^8R^9$, $-SO_2NR^8R^9$, or $NR^{10}R^{11}$ wherein R^7 is optionally substituted lower alkyl, R^8 and R^9 are independently hydrogen or optionally substituted lower alkyl or aryl, or together form a heterocyclic ring with the amide nitrogen atom, R^{10} is hydrogen or optionally substituted lower alkyl, aralkyl, aryl or acyl, R^{11} is aryl or R^{10} and R^{11} taken together may form a heterocyclic ring with the nitrogen atom the ring optionally containing further hetero atoms, R^4 may be the same as R^3, R^5 or R^6 except that when R^4 is $-NR^{10}R^{11}$, R^{10} may be hydrogen, lower alkyl, aralkyl, aryl or acyl and R^{11} may be aryl or with R^{10} may form a heterocyclic ring together with the nitrogen atom, or if R^{10} is not acyl, R^{11} may be acyl, Y is O-lower alkyl or $-NR^{12}R^{13}$ where R^{12} and R^{13} are independently optionally substituted alkyl or aryl groups, or can form a heterocyclic ring with the amide N atom and when Y is $-NR^{12}R^{13}$, R^4 can be the same as R^3, R^5 and R^6 in all respects, and X is an anion.

Examples of R^1 include hydrogen, methyl, ethyl, propyl, and n-butyl. R^1 is preferably hydrogen or lower alkyl, i.e. an alkyl group containing from 1 to 4 carbon atoms.

Examples of R^2 include phenyl, 1,3,5-trimethylphenyl, *o*-, *m*- or *p*-chlorophenyl, *o*, *m*- or *p*-tolyl.

Examples of R^3, R^4, R^5 and R^6 include hydrogen, methyl, benzyl, phenyl,

acetyl, benzoyl, methoxy, ethoxy, phenoxy, chlorine, bromine, cyano, nitro, ethoxycarbonyl, carbo-N,N-diethylamide, sulphon-N,N-diethylamide, diethylamino, ethylamino, amino, acetylamino, benzylamino, dibenzylamino, anilino, N-methylanilino, p-toluidino, morpholino, piperidino and pyridin-1-yl.

Examples of R^7 include methyl, ethyl, propyl, isopropyl, n-butyl and tert.-butyl and benzyl.

Examples of R^8 and R^9 include hydrogen, methyl, ethyl, and when taken together with the N atom piperidinyl and morpholinyl.

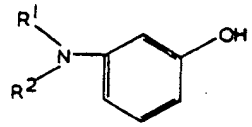
Examples of R^{10} include methyl, ethyl, propyl and n-butyl, and where R^{10} and R^{11} are taken together with the N atom, examples include piperidinyl and morpholinyl. Phenyl and *o*-chlorphenyl are examples of R^{11}.

Examples of Y includes methoxy, ethoxy, phenoxy, benzyloxy, dimethylamino and diethylamino.

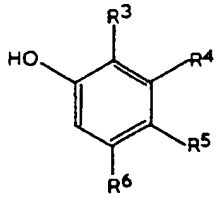
By the term lower alkyl is meant an alkyl group with from one to four carbon atoms.

Examples of the anion X include chloride, bromide, iodide tetrachlorozincate, bisulphate, nitrate, bisulphate, sulphate, sulphamate, phosphate or borate or organic anions such as acetate, propionate, acetate, methosulphate, methylsulphate and p-tolylsulphonate. In those cases where the anion is polyvalent the dyestuffs will contain a corresponding molar proportion of the cationic part of the dyestuff.

The dyestuffs used in the present invention may be obtained by known methods for example by condensation of phthalic anhydride or a substituted derivative thereof with the appropriate optionally substituted meta-aminophenol of the general formula



wherein R^1 and R^2 are as hereinbefore defined, followed by condensation of the product with a compound of the formula



wherein R^3 to R^6 are as hereinbefore defined, followed by conversion of the carboxylic acid group to a group —COY and solubilisation by salt formation. Dyestuffs of this type have been described in the art.

Colouration of the polymeric material may be carried out by applying the dyestuff from aqueous solution.

The polymeric materials may be for example in the form of tapes, fibres, films, threads or textile materials generally.

The colouration process of the present invention may be applied to polymeric materials generally including polyamides and polyesters, in particular acid modified polyamides and polyesters but is considered especially valuable for application to the dyeing or printing of polyacrylonitrile and copolymers containing acrylonitrile residues. Blends of different polymeric materials either synthetic or natural may also be used.

The colouration process may be carried out by applying the dyestuff from acid, neutral or slightly alkaline aqueous dyebaths, i.e. at a pH of from 3 to 8, at temperatures between 40°C and 120°C preferably between 80°C and 120°C or by printing techniques. Printing techniques which may be used include the known methods in which the usual thickeners and optional printing aids are added and

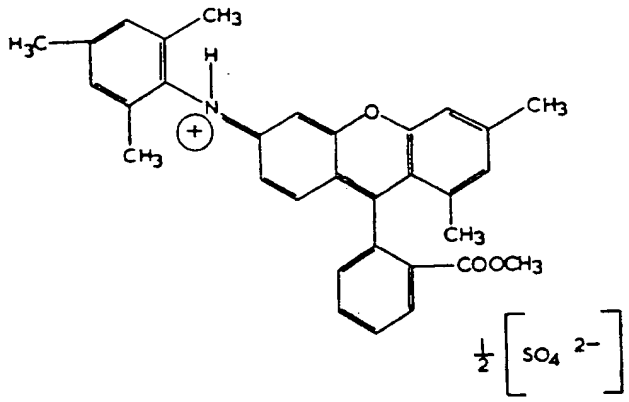
final fixation of the dyestuff takes place in the usual manner, for example by steaming.

The dyeings give bright shades of excellent fastness to light, washing and heat treatment.

The invention is illustrated by the following examples in which all parts and percentages are by weight except where otherwise stated.

Example 1.

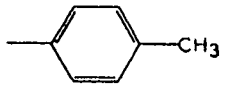
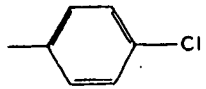
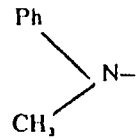
100 Parts of polyacrylonitrile fibre are immersed in 3000 parts of water containing 1 part of a dyestuff of formula:—

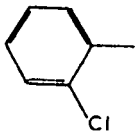
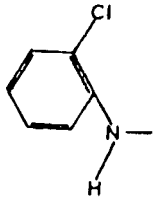
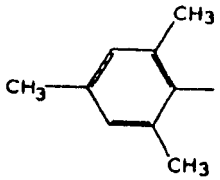
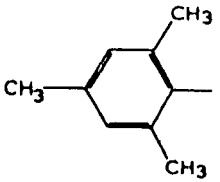
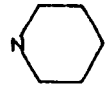


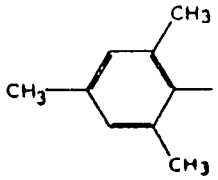
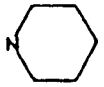
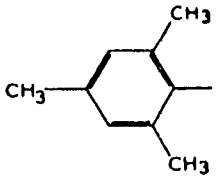
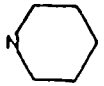
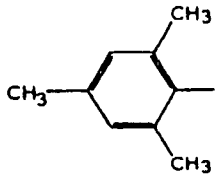
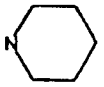
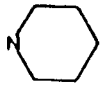
1 part of sodium acetate and 0.6 parts of acetic acid at 60°. The temperature is raised slowly to 100°C, and dyeing continued at this temperature for 90 minutes. The resulting dyeing has a reddish-yellow shade and good fastness to light, washing and heat treatment.

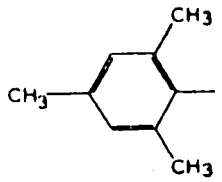
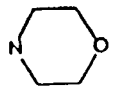
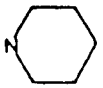
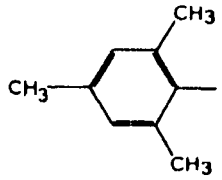
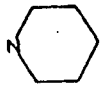
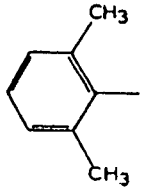
Examples 2—29

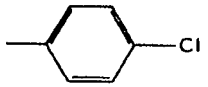
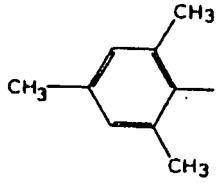
Examples 2—29 are further examples of dyestuffs of Formula I which can be applied in the process of the present invention by the method of Example 1. The substituents are tabulated below and the table includes the shades obtained when the dyestuffs are applied to a polyacrylonitrile textile material.

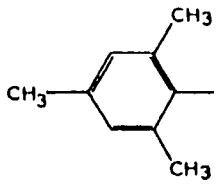
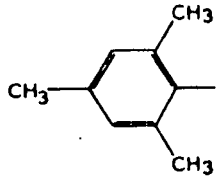
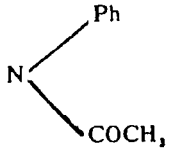
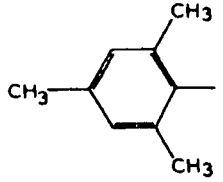
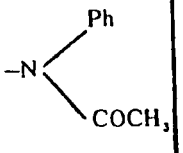
Example	R_1	R_2	R_3	R_4	R_5	R_6	Y	X^-	Shade on poly-acrylonitrile
2	H	Ph	H	CH_3	Cl	H	OCH_3	Cl^-	Red
3	H	Ph	H	H	NO_2	H	OCH_3	$\frac{1}{2}[SO_4^{2-}]$	Reddish-yellow
4	H	Ph	Cl	H	Cl	H	OC_2H_5	Cl^-	Red
5	CH_3	Ph	Cl	H	Cl	H	OC_2H_5	Cl^-	Bluish-red
6	CH_3		Cl	H	Cl	H	OC_2H_5	Cl^-	Bluish-red
7	CH_3		Cl	H	Cl	H	OC_2H_5	Cl^-	Bluish-red
8	CH_3	Ph	CH_3	H	CH_3	H	NEt_2	CH_3COO^-	Red
9	CH_3	Ph	H		H	H	OCH_3	Cl^-	Blue

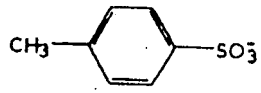
Example	R_1	R_2	R_3	R_4	R_5	R_6	Y	X^-	Shade on poly-acrylonitrile
10	H		H		H	H	OCH_3	$\frac{1}{2}[SO_4^{2-}]$	Scarlet
11	H		H	H	NHEt	H		Cl^-	Blue-grey
12	H		H	H	NEt_2	H		Cl^-	Dull green

Example	R_1	R_2	R_3	R_4	R_5	R_6	Y	X^-	Shade on polyacrylonitrile
13	H		H	H	$N(CH_2C_6H_5)_2$	H		Cl^-	Dull green
14	H		H	H	$NHCOCH_3$	H		Cl^-	Bluish-red
15	H		H	H		H		Cl^-	Dull green

Example	R_1	R_2	R_3	R_4	R_5	R_6	Y	X^-	Shade on polyacrylonitrile
16	H		H	H		H		Cl^-	Black
17	H		H	H	NHPh	H		Cl^-	Black
18	CH_3		H	CH_3	H	CH_3	$N(CH_3)_2$	CH_3COO^-	Orange

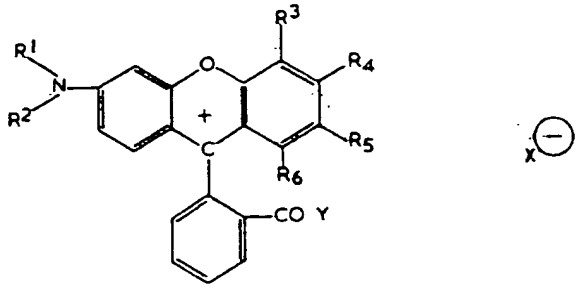
Example	R_1	R_2	R_3	R_4	R_5	R_6	Y	X^-	Shade on polyacrylonitrile
19	C_2H_5	Ph	H	CH_3	H	CH_3	$N(CH_3)_2$	CH_3COO^-	Bluish-red
20	n-C_3H_7	Ph	H	CH_3	H	CH_3	$N(CH_3)_2$	CH_3COO^-	Bluish-red
21	CH_3		H	CH_3	H	CH_3	$N(CH_3)_2$	CH_3COO^-	Bluish-red
22	H		NH_2	H	CH_3	H	$N(CH_3)_2$	Br^-	Red

Example	R_1	R_2	R_3	R_4	R_5	R_6	Y	X^-	Shade on polyacrylonitrile
23	H		H	CH_3	NH_2	H	$N(CH_3)_2$	Cl^-	Rubine
24	H		H	H		H	OCH_3	Cl^-	Red
25	CH_3		H	H		H	OCH_3	CH_3COO^-	Bluish-red

Example	R_1	R_2	R_3	R_4	R_5	R_6	Y	X^-	Shade on polyacrylonitrile
26	H	Ph	H	H	Br	H	OCH_3		Red
27	H	Ph	H	CH_3	$N(CH_3)_2$	H	OCH_3		Dark red
28	H	Ph	H	OCH_3	H	OCH_3	OCH_3		Red
29	C_2H_5	Ph	H	Cl	H	Cl	OPh	Cl^-	Red

WHAT WE CLAIM IS:—

1. A process for the colouration of synthetic polymeric materials which comprises applying thereto a dyestuff of the general Formula I



(I)

wherein R^1 is hydrogen or an optionally substituted alkyl group, R^2 is an optionally substituted aryl group, R^3, R^5 and R^6 are independently chosen from hydrogen, optionally substituted alkyl, aralkyl or aryl groups, acyl, alkoxy, aryloxy, halogen, cyano, nitro, or a group of the formula $—COOR^7$, $CONR^8R^9$, $—SO_2NR^8R^9$ or $NR^{10}R^{11}$ wherein R^7 is optionally substituted lower alkyl, R^8 and R^9 are independently hydrogen or optionally substituted lower alkyl or aryl, or together form a heterocyclic ring with the amide nitrogen atom, R^{10} is hydrogen or optionally substituted lower alkyl, aralkyl, aryl or acyl, R^{11} is aryl or R^{10} and R^{11} taken together may form a heterocyclic ring with the nitrogen atom the ring optionally containing further hetero atoms, R^4 may be the same as R^3, R^5 or R^6 except that when R^4 is $—NR^{10}R^{11}$, R^{10} may be hydrogen, lower alkyl, aralkyl, aryl or acyl and R^{11} may be aryl or with R^{10} may form a heterocyclic ring together with the nitogen atom, or if R^{10} is not acyl, R^{11} may be acyl, Y is O-lower alkyl or $NR^{12}R^{13}$ where R^{12} and R^{13} are independently optionally substituted alkyl or aryl groups, or can form a heterocyclic ring with the amide N atom and when Y is $NR^{12}R^{13}$, R^4 can be the same as R^3, R^5 and R^6 in all respects, and X is an anion.

2. A process as claimed in Claim 1 wherein R^1 is hydrogen or lower alkyl.

3. A process as claimed in Claim 1 or Claim 2 wherein the dyestuff is applied to a polymeric material from aqueous solution.

4. A process as claimed in any one of the preceding claims wherein the polymeric material is polyacrylonitrile or a copolymer containing acrylonitrile residues.

5. A process as claimed in any one of the preceding claims wherein the dyestuff is applied from an acid, neutral or slightly alkaline aqueous bath at a pH of from 3 to 8 at a temperature between 40° and 120°C.

6. A process as claimed in Claim 5 wherein the temperature is from 80° to 120°C.

7. A process as claimed in any one of the preceding claims wherein the dyestuff is applied by a printing technique.

8. A process according to Claim 1 with reference to any one of Examples 1 to 29.

9. Polymeric materials whenever coloured by a process as hereinbefore described and claimed.

DONALD LEES,
Agent for the Applicants.

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